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7 **Nanostructured Titanium Nitride as a Novel Cathode for**
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10 **High Performance Lithium/Dissolved Polysulfide**
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14 **Batteries**
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20 Negar Mosavati ^a, Venkateswara Rao Chitturi ^a, Steven O. Salley ^a, K. Y. Simon Ng ^{a,*}
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22 ^a *Department of Chemical Engineering and Materials Science, Wayne State University,*
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24 *Detroit, MI 48202, USA*
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35 *** Corresponding author:** K. Y. Simon Ng;
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37 E-mail address: sng@wayne.edu; Fax: +1 313 577 8171; Tell: +1 313 577 3805
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Abstract

Lithium–sulfur (Li-S) batteries could potentially revolutionize the rechargeable battery market due to their high energy density and low cost. However, low active material utilization, electrode volumetric expansion and a high rate of capacity fade due to the dissolution of lithium polysulfide intermediates in the liquid electrolyte are the main challenges facing further Li-S battery development. Here, we enhanced Li-S batteries active material utilization and decreased the volumetric expansion by using the lithium/dissolved polysulfide configuration. Moreover, a novel class of cathode materials, Titanium Nitride (TiN), was developed for polysulfide conversion reactions. The surface chemical environment of the TiN has been investigated by X-ray photoelectron spectroscopy (XPS) analysis. The existence of S-Ti-N bonding at the cathode electrode surface was observed, which indicates the strong interactions between TiN and polysulfides. Therefore, the TiN electrode retains the sulfur species on the cathode surface, minimizing the active material and surface area loss and consequently, improves the capacity retention. The resultant cells demonstrated a high initial capacity of 1,524 mAh g⁻¹ and a good capacity retention for 100 cycles at a C/10 current rate.

Keywords

Lithium sulfur battery; Dissolved Polysulfide; Cathode material; Titanium Nitride

1. Introduction

Advances in portable electronic devices and electric vehicles require efficient electrical energy storage systems, such as rechargeable batteries with high energy density and long lasting cycle performance. Among the most promising energy storage systems, lithium-sulfur (Li-S) batteries could significantly improve the rechargeable battery market due to their high energy density of $2,600 \text{ Wh kg}^{-1}$ and theoretical capacity of $1,675 \text{ mAh g}^{-1}$ [1]. In addition, sulfur is environmentally friendly and has a low cost [1-3]. However, there are some challenges facing Li-S battery development, such as: low active material utilization, high self-discharge products, volumetric expansion associated with intermediate products, and high rate of capacity fade due to the dissolution of lithium polysulfide intermediates in liquid electrolyte, which also increase the redox shuttle reactions and lithium corrosion [1, 3, 4]. In order to overcome these obstacles, many studies have attempted to develop various cathode materials such as functionalized carbon materials, graphene oxides, and conducting polymers with high surface area and porosity [4-9]. These materials were designed to enhance Li-S cell capacity retention due to their ability to maintain polysulfides by physisorption, or to chemisorb lithium polysulfides because of their hydrophilic nature [10, 11]. Metal oxides, such as TiO_2 , Al_2O_3 and SiO_2 as well as metal sulfides, such as TiS_2 and ZrS_2 were also reported to adsorb lithium polysulfides and reduce redox shuttle reactions in Li-S batteries [12-16]. In addition, Ti_4O_7 has been demonstrated to enhance the redox chemistry and cyclability due to its sulfiphilic surface and good electron conductivity [17].

On the other hand, a dissolved polysulfides configuration has been reported to have high reaction activity and sulfur utilization compared to conventional Li-S batteries [18-20]. Barchasz et al. demonstrated that the discharge capacity could be increased to up to 1,400

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4 mAh g⁻¹ at a low rate of C/100, using carbon foam and dissolved 0.5 mol L⁻¹ Li₂S₆-Li₂S₈
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6 catholyte. However, its capacity decreases to 1,200 mAh g⁻¹ within 10 cycles [21].
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8 Demir-Cakan et al. showed the capacity performance of Li₂S₅ with a Ketjen Black carbon
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10 cathode at C/10 rate. Their results show an almost 1,200 to 500 mAh g⁻¹ capacity, and 500 to
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12 300 mAh g⁻¹ capacity deactivation for 0.3 and 0.1 M Li₂S₅ catholyte concentrations,
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14 respectively, within 70 cycles [22]. The low performance of carbon materials is mainly due to
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16 their poor adsorption properties toward lithium polysulfides. Therefore, in order to take full
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18 advantage of dissolved polysulfide Li-S battery, it is important to enhance its capacity
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20 retention and cycle lifetime using efficient cathode materials. The studies that emerged from
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22 the reported works indicate that the battery performances centred mainly on the development
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28 Based on our experiences in improving the battery performances using nanostructured
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30 electrodes [20, 23, 24], we investigated transition metal nitrides as a new class of cathode
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32 materials and demonstrated the superior performance in a Li/dissolved polysulfide battery
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34 configuration for the first time. Transition metal nitrides are well known materials for
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36 supercapacitors and lithium-ion batteries due to their high reversible insertion and extraction
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38 of ionic species and the capability of storing lithium by the intercalation mechanism [25-30].
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40 Different types of metal nitride such as TiN [31], VN [32], Mo₂N [33, 34], Zn₃N₂ [35], Ni₃N [36],
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42 NbN [37], have been demonstrated as efficient electrode materials for lithium-ion batteries
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44 and supercapacitors. Among the metal materials, titanium nitride (TiN) has unique properties
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46 such as high electrical conductivity (4,000–55,500 S cm⁻¹) [37] and thermodynamic stability
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48 and corrosion resistance due to the presence of a triple covalent bond between titanium and
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50 nitrogen. In this work, titanium nitride (TiN) is investigated as a novel cathode material for
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Li/dissolved polysulfide batteries since it can adsorb lithium polysulfides effectively and transfer electrons in a facile manner. As revealed by X-ray photoelectron spectroscopy (XPS) analysis, sulfur interacts with TiN nanoparticles during the discharge process, and resulted in S-Ti-N, which retains the sulfur species on the cathode surface. The adsorbed higher order polysulfide species undergo reduction to lower order polysulfides by transfer of electrons from the TiN electrode. As a result, the active material and surface area loss were reduced and the capacity and capacity retention of the cell were enhanced.

2. Experimental Details

2.1 Preparation of Titanium Nitride

Titanium oxide powder (TiO_2 , 10-25 nm size, US Research Nanomaterials) was used as precursor. The powder was first loaded into a zirconia boat and placed in a tubular reactor, which was connected to the gas feed system. Initially, the reactor was purged using 150 mL/min Argon (Ar) gas for 1h; followed by 200 mL min^{-1} pure NH_3 gas for 30 min to stabilize the gas flow. The reactor was then heated to 250 °C, in 8 h, held for 40 min, then raised to 1000 °C over 3h and maintained for 1h. The furnace cooled down to room temperature followed by flowing 150 mL min^{-1} Ar gas overnight.

2.2 Fabrication of electrodes and Cell assembly

The cathode slurry was prepared by adding 10 wt% of Poly (vinylidene fluoride) PVDF, as binder and N-methyl pyrrolidinone (NMP) as solvent to the cathode materials (TiN). The slurry was then coated on aluminum (Al) foil (0.1 mm thick) and dried at 80 °C under vacuum for 12h.

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4 Elemental sulfur S₈, lithium sulfide Li₂S, Bis(trifluoromethane)sulfonimide lithium salt
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6 LiN(SO₂CF₃)₂, LiTFSI, triethylene glycol dimethyl ether (TG₃), were purchased from Aldrich
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8 and used as received. Catholyte solutions with 0.2, 0.6, 0.8 M Li₂S₈, 0.1 M LiTFSI, and 1 M
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10 LiNO₃ were prepared by stirring appropriate amounts of S₈ and Li₂S into TG₃ at 70 °C for 8 h.
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14 10 µL of catholyte solution was added on the positive electrodes with 7 mg cm⁻² electrode
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16 loading. Coin cells (CR2032) were assembled using polypropylene separator (Celgard 2400)
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18 and lithium foil anode inside the Ar-filled glove box.
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23 24 **2.3 Characterization and Electrochemical measurements**

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26 The phase purity of the cathode electrode materials was characterized using a Rigaku
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28 Miniflex 600 X-Ray Diffractometer. Cathode material morphology was characterized with field
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30 emission scanning electron microscopy (JEOL 7600F, FESEM). The specific surface areas of
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32 the electrode materials were measured by Braunauer-Emmet-Teller (BET) multimolecular
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34 adsorption method (Micromeritics Tristar II surface area/porosimeter). Galvanostatic
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36 discharge-charge tests were conducted using a Maccor Model 4200 Automated Test System
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38 between the voltage range of 1.5 to 3 V and 1.8 to 3 V (vs. Li/Li⁺) at room temperature. Cyclic
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40 voltammetry and electrochemical impedance spectroscopy (EIS) measurements were applied
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42 using a Gamry potentiostat reference 3000. The voltammetry was performed at a scan rate of
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44 0.05 mV s⁻¹, and a voltage range of 3 to 1.5 V (vs. Li/Li⁺). EIS were recorded between 1 MHz
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46 and 0.1 Hz, and AC amplitude of 10 mV at room temperature.
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54 55 **3. Results and discussion**

56 57 **3.1 Structure and morphology**

Nanostructured TiN was prepared by heating titanium oxide (TiO_2) under an ammonia atmosphere. Crystal structure of the prepared TiN analyzed by X-ray diffraction (XRD) (Fig. 1a) presents five diffraction peaks of TiN (111), (200), (220), (311) and (222). The positions and intensities of TiN diffraction peaks can be indexed to the face-centered cubic phase structure of TiN (JCPDS file no. 38-1420) with lattice constant $a = 0.424$ nm (Fig. 1b). Crystallite size was calculated to be 16 nm from broadening of the diffraction peak using Scherrer's equation [38].

Fig. 1. (a) Powder XRD pattern of TiN, (b) Face-centered cubic structure of TiN (blue and red spheres represent Ti and N atoms respectively), (c) SEM image of TiN powder, (d) TEM image of TiN powder, (e) SAED pattern of TiN.

Scanning electron microscopic (SEM) image depicted agglomeration of TiN nanoparticles (Fig. 1c). Transmission electron microscopic (TEM) image showed the connectivity between irregular shaped grains, imparting electronic conductivity (Fig. 1d). Average particle size was found to be 30 nm from the measurement of about 100 particles found in an arbitrarily chosen area of the enlarged microscopic images. Selected area electron diffraction (SAED) pattern further confirmed the polycrystalline nature of the sample (Fig. 1e). The d-spacing from inner to outer can be indexed to the (111), (200), (220), (311) and (222) planes of a cubic phase, which is in a good agreement with the XRD results. The BET surface area of TiN was measured to be $22.1 \text{ m}^2 \text{ g}^{-1}$ using BET sorptometry.

3.2. Electrochemical performance

The electrochemical performance of the TiN cathode at a 0.1 C rate was examined with an Al foil without TiN coating, and TiN coated Al foil with loadings of (3, 6 and 7 mg cm^{-1}) and with a 0.2 M Li_2S_8 catholyte concentration. The results are been presented and discussed in (Fig. S1 of the Electronic Supplementary Information). In addition, the effect of Li_2S_8 catholyte concentrations on Li-S battery performance with TiN cathode has been investigated. It is observed that the capacity and cycle performance of the Li-S battery can be influenced by the catholyte concentration. The capacity fade of 52%, 47%, and 33% after 100 cycles was calculated for 0.2, 0.6, and 0.8 M Li_2S_8 concentrations, respectively. Although cells with 0.6 and 0.8 M concentrations of Li_2S_8 revealed more stable performance, their capacities stay lower than the cell with 0.2 M Li_2S_8 during 100 cycles. This could be due to the high Li_2S_8 catholyte concentration, which reduces the Li ion diffusion into the cathode electrode and wettability of the electrode surface by the electrolyte. It was also reported that increasing

viscosity might lead to higher active material loss as a result of the insoluble lithium polysulfides (Li_2S_2 , and Li_2S) formation, which were detected on the surface of cathode electrode [39, 40]. Insoluble lithium polysulfide deposition during cycling can cause capacity fading and lower cyclability, thus, irrespective of different catholyte concentration, similar capacities (around 700 mAh g^{-1}) were observed after 100 cycles.

Fig. 2. (a) Cycling performances of the battery with TiN cathode and different Li_2S_8 catholyte concentrations, (b) Cyclic voltammograms recorded for TiN cathode with 0.2 M Li_2S_8 catholyte concentration, at a scan rate of 0.05 mV s^{-1} .

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4 In order to have a better understanding of TiN electrode activity towards the polysulfide
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6 conversion reactions, cyclic voltammetry was performed for a cell with a 0.2 M Li_2S_8 catholyte
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8 concentration at a scan rate of 0.05 mV s^{-1} (Fig. 2b). The typical sulfur redox reactions with
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10 one oxidation and two reduction peaks were observed for all cycles. In general, reduction of
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12 Li_2S_8 to Li_2S occurs through a series of intermediate Li_2S_x species ($2 < x < 8$) at different
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14 potentials [19], The higher voltage cathodic peak corresponds to the reduction of dissolved
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16 Li_2S_8 in the catholyte on the surface of the cathode to soluble higher order lithium polysulfide
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18 Li_2S_x ($4 < x < 6$), and the lower voltage cathodic peak represents the further reduction of
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20 polysulfides to insoluble lithium sulfides (Li_2S_2 and Li_2S) [19]. The final region that occurs
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22 lower than 1.8 V potential is associated with the deeper reduction of Li_2S_2 to Li_2S , both of
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24 which are insoluble in most electrolyte media [3, 19, 20]. Therefore, by limiting the lower
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26 voltage to 1.8 V, with less Li_2S formation, active material and active surface area loss should
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38 3.2.2 Effect of voltage limit

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40 Fig. 3a and 3b show the galvanostatic discharge-charge (GDC) profiles of the TiN electrode
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42 at 0.1 C rate, with 0.2 M Li_2S_8 catholyte concentration and voltage limits of 1.5-3.0 V and 1.8-
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44 3.0 V, respectively. They both demonstrated two plateaus in the voltage range of 2.45 and
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46 2.0 V (vs. Li/Li^+). The higher and lower voltage plateaus correspond to the conversion of Li_2S_8
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48 to higher order (Li_2S_n $n > 4$) and lower order lithium polysulfide (Li_2S_n $n < 4$), respectively. These
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50 two plateaus correspond to 25% and 75 % of the practical capacity. By limiting the lower
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52 voltage limit to 1.8, a small percent of capacity was confined. However, the overall capacity
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54 was enhanced. Fig. 3c shows the performance of the cell with a narrow voltage limit of 1.8 to
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3.0 V, which exhibits almost 30% higher capacity retention compared to the cell with voltage limit of 1.5 to 3.0 V. The capacity of 726 mAh g⁻¹ sulfur after 100 cycles at 0.1 C rate (1.5 to 3.0 V) is comparable to reported capacities for lithium/dissolved polysulfide systems with the same voltage limit, such as capacity of 789 mAh g⁻¹ and 600 mAh g⁻¹ after 100 cycles for Pt/graphene cathode with 0.2 M Li₂S₈ catholyte concentration [24], and vertically-aligned carbon nanotubes with 0.3 M Li₂S₆ concentration [41] respectively. However, with a narrower voltage limit (1.8 to 3.0 V), a higher capacity, 1,040 mAh g⁻¹ sulfur after 100 cycles at 0.1 C rate, was observed.

Fig. 3. Effect of voltage limit on the Li/dissolved polysulfide battery performances at 0.1 C rate: (a) GDC profiles in the voltage limit 1.5-3.0 V (b) GDC profiles in the voltage limit 1.8-3.0 V, (c) Cycling performances.

AC impedance measurements between the 10th and 100th cycles (Fig. S2) also suggest that the charge transfer resistance at the TiN/electrolyte interface increased almost 37 Ω for the voltage limit of 1.5 V; while only a 5 Ω increase was observed for the voltage limit of 1.8 V (Table. S1). The increase in resistance can be attributed to the passivation layer formation on the TiN electrode surface, which decreases the conductive surface area of the electrode.

Fig. 4. Effect of voltage limit on the Li/dissolved polysulfide battery performances at 1.0 C rate: (a) GDC profiles in the voltage limit 1.5-3.0 V (b) GDC profiles in the voltage limit 1.8-3.0 V, (c) Cycling performances.

Cycling performance of the cells was also measured at 1.0 C and the results are plotted in Fig. 4. Capacity retention of the cells with 1.5-3.0 V and 1.8-3.0 V limits at 1.0 C rate per 100

cycles were measured to be 55% and 83%, respectively. GDC profiles at a 1.0 C rate presented in Fig. 4a indicate that insoluble polysulfides (Li_2S_2 and Li_2S) started to form almost at the voltage of 1.5. In contrast, at 0.1 C rate (Fig. 3a), significant amount of insoluble polysulfides were formed. Therefore, restricting the lower voltage limit to 1.8 V at the 1.0 C rate did not significantly reduce solid polysulfide formation, however, it reduced the overall capacity.

Fig. 5. Rate capability at different current rates in the voltage limit 1.8-3.0 V.

In addition, the rate capability of the TiN electrodes was studied at different C rates for two cells with the same configuration (Fig. 5). The C rate is based on the theoretical capacity of sulfur ($C = 1675 \text{ mAh g}^{-1} \text{ sulfur}$). The cells were first subjected to a low 0.1 C rate to obtain stable nominal capacity. Subsequent cycling was performed at higher current rates of 0.2, 0.5, 1.0, and 2.0 C each for 10 cycles. Finally, it was reverted to 0.1 C for 10 additional cycles. Interestingly, cell capacity retention increases as the C rate increases. The results

show a very low rate of capacity fade (~ 1%) at the 2.0 C rate, compared to 6 percent at the 0.1 C rate. Although the specific capacity decreases with increasing cycle numbers, the cell recovered most of its capacity when the current rate was returned back to 0.1 C.

3.3 Morphological changes of the cathodes

Microstructural changes of the TiN electrodes during cycling were ascertained by SEM (Fig. 6a-c). After the first discharge process to 1.8 V, some precipitation was detected on the electrode surface, which formed a thin passivation layer on the TiN surface (Fig. 6a and S3a). This precipitation appeared to be reduced after the first charging process to 3.0 V (Fig. 6b and S3b). However, after the 100th charge, besides having more passivation layer formed on the electrode surface, the grains size seems to be larger, which could be due to particle agglomeration or coverage of particles with precipitated Li₂S₂, Li₂S and S₈ (Fig. 6c).

In order to identify the surface chemical environment of the TiN composites after cycling, X-ray photoelectron spectroscopy (XPS) analysis was conducted on TiN electrodes extracted from cells at the end of the first charged and discharged states. The deconvoluted spectra in the S2p region are presented in Fig. 6d-e. When the cell was discharged to 1.8 V, peak binding energies of 160 and 161.2 eV suggested Li₂S and Li₂S₂ were formed, respectively [42-44]. The intensity of the Li₂S₂ peak is stronger because the voltage limit of 1.8 V prevents further Li₂S formation. After the first charge, no Li₂S peak was observed, which indicates that Li₂S was completely oxidized back to higher order lithium polysulfides. However, there is still some Li₂S₂ precipitation detected on the TiN cathode surface. Moreover, long chain polysulfides Li₂S_n (n≥4) were detected at 162.6±0.1 eV [42-44] for both first discharge and charge status, consistent with incomplete redox reactions before the formation of solid electrolyte interlayer

(SEI). SEI layer, which has been reported to form mostly during the first cycle on the Li anode, prevents the continuous electron transfer from the Li anode to dissolved polysulfides and suppresses redox shuttle reactions [45].

Fig. 6. Post-mortem analysis of the TiN electrodes; (a,d) First discharge, (b,e) First cycle in charged state, (c,f) 100th cycle in charged state. First and second columns are corresponded to the SEM images and deconvoluted XPS S2p spectra of the TiN electrodes. Original and fitted XPS data are represented with black and red lines respectively.

A strong peak of Li_2S in addition to Li_2S_2 peak was detected on the XPS spectra of the electrode after the 100th charge, which explains the capacity fading of the Li-S cell after 100 cycles. The peaks with the binding energy of 167 ± 0.2 eV, which can be attributed to the -S-O bonding in $-\text{SO}_3$ and $-\text{SO}_2$ species, can be found in all samples. These species are originated from the electrolyte [43, 46]. In addition to the long chain polysulfides detected in the S2p spectrum of the first discharge state, an additional sulfur peak was observed at 163.1 eV. This peak, which is sited within the range of Ti-S binding energy, can be attributed to the S-Ti-N bond. To confirm the TiN- Li_2S_8 interaction, 100 mg of TiN was mixed with 5 ml of 0.01 M catholyte solution and stirred (Fig. S4). The catholyte color changed from bright yellow-green to colorless within 30 min, which indicates that the polysulfides were adsorbed by TiN powder. The adsorbed higher order polysulfides were reduced by transfer of electrons from the TiN electrode and converted to the lower order polysulfides (Li_2S_2 and Li_2S). In addition, as a result of reversible S-Ti-N binding interactions, the active material loss due to lower order polysulfides precipitation decreases.

4. Conclusions

In summary, we have shown that TiN is a promising cathode material for advanced Li/dissolved polysulfide batteries. We demonstrate that changing the lower voltage limit from 1.5 V to 1.8 V at 0.1 C rate highly enhances the cycling performance of the Li-S battery due to decreasing the insoluble polysulfides formation on the cathode electrode. Furthermore, the existence of S-Ti-N bonding at the electrode surface observed by XPS analysis is indicative of strong interactions between polysulfides and TiN. This could effectively mitigate the insoluble lithium sulfide formation on the cathode surface, which minimizes the active

material and surface area loss and improves the capacity retention. The resultant cells deliver high capacity of almost 1,040 mAh g⁻¹ sulfur after 100 cycles at 0.1 C rate.

Acknowledgment

Financial support from the Department of Energy (Grant DEEE0002106) is gratefully acknowledged.

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